

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

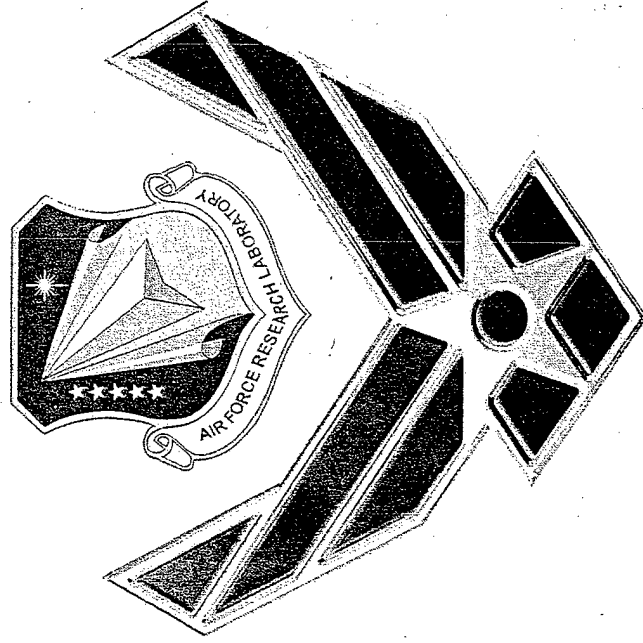
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 02/12/2004		2. REPORT TYPE Technical Paper (View Graph)		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Update in Ionic Liquids Research				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Greg Drake, Tommy Hawkins,				5d. PROJECT NUMBER 2303	
				5e. TASK NUMBER M2C8	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB, CA 93524-7048				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB, CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-VG-2004-030	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES AFOSR Ionic Liquids Workshop Tampa, FL 7-8 March 2004					
14. ABSTRACT <div style="text-align: center; font-size: 2em; border: 1px solid black; padding: 10px; margin: 20px auto; width: 80%;">20040503 190</div>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified			A	32	Linda Talon
b. ABSTRACT Unclassified					19b. TELEPHONE NUMBER (include area code) (661) 275-5283
c. THIS PAGE Unclassified					

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Best Available Copy

Update in Ionic **Liquids Research**



Greg Drake and Tommy Hawkins

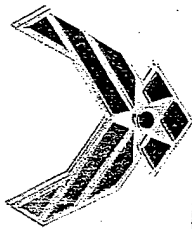
AFRL/PRSP

AFOSR Ionic Liquids Workshop

March 7 & 8, 2004

Tampa, FL

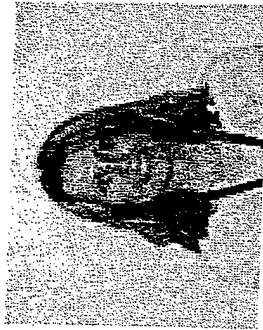
Distribution Statement A: Public Release, Distribution unlimited.



AFRL Ionic Liquids



Those involved in this work



Ms. Kerri Tollison
Synthesis and
Characterization



Greg Kaplan
Synthesis and
Characterization



Jerry Boatz
Theoretical
Calculations



Jeff Mills
Theoretical
Calculations



Leslie Hall
Synthesis &
x-ray work



Ashwani Vij
X-ray
crystallography

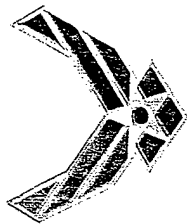


Tommy Hawkins
6.2 Propellant
Development

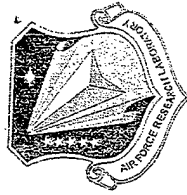


Greg Drake
6.1 Research
Synthesis

Distribution A: Public Release, Distribution unlimited



AFRL Ionic Liquids



HOW WE GOT TO WHERE WE ARE

- SIMPLE SALTS USING PROTIC ACIDS

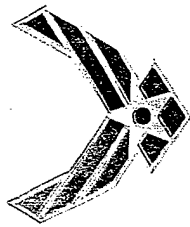
- OPEN CHAIN WORK
HYDROGEN BONDING EFFECTS

HYDRAZINE ANALOGUES

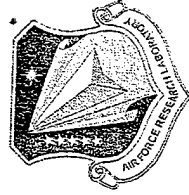
SOME SIMPLE AMINES

- HETEROCYCLIC APPROACH

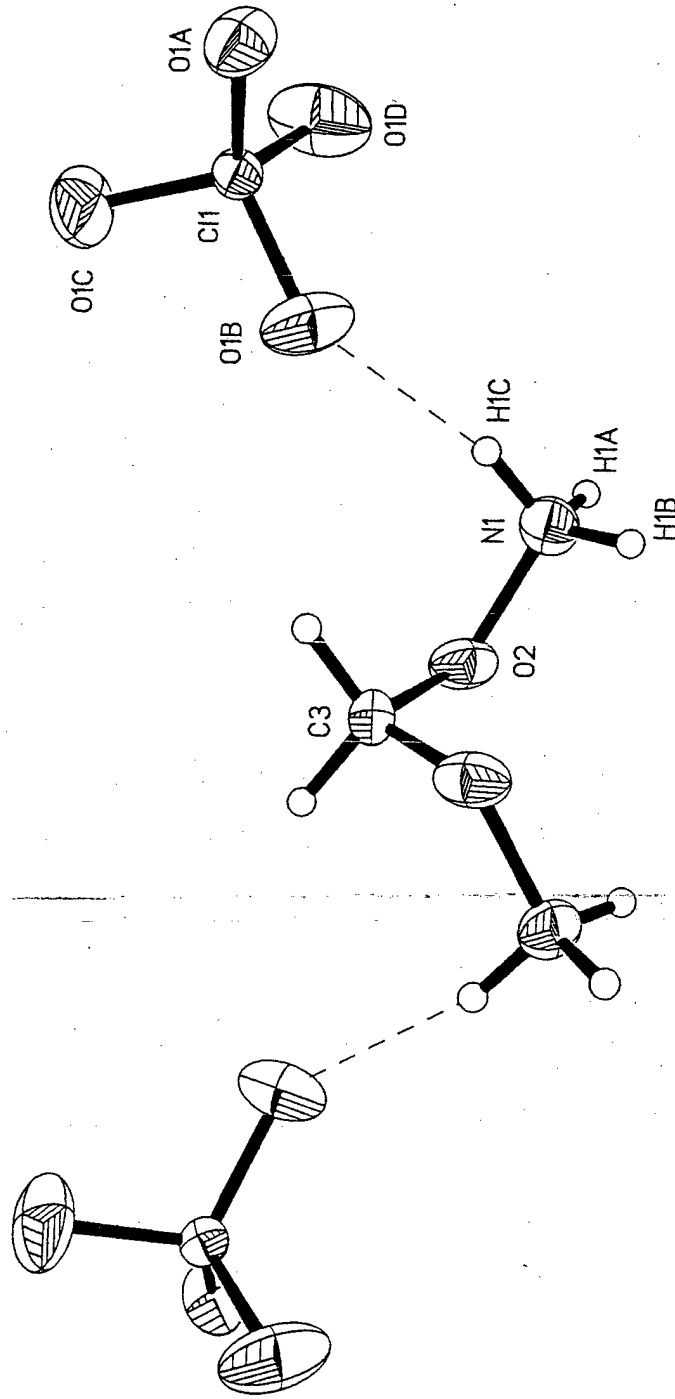
SHAPE CONSIDERATIONS



AFRL Ionic Liquids

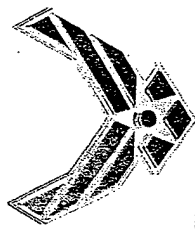


- Oxyamine, $-O-NH_2$, is analogue to hydrazine linkage $-NH-NH_2$
- $CH_2(O-NH_2)_2$ Explored at Edwards in late 1960's (Claude Merrill)
- Reinvestigation of mono- and di- salts
- Several of the salts met the definition of an ionic liquid
- Treacherous! Sensitive to mechanical stimuli! Explode unexpectedly!

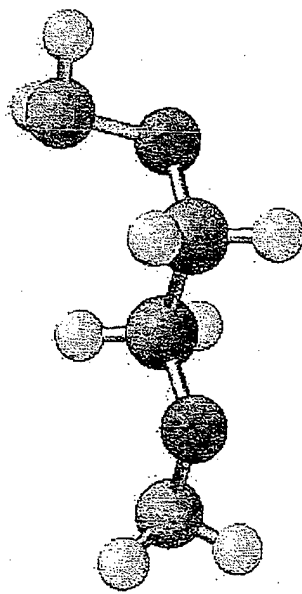
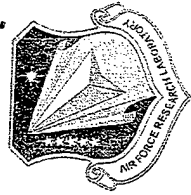


Tollison, K.; Drake, G.; Hawkins, T.; Brand, A.; McKay, M.; Ismail, I.; Merrill, C.; Petrie, M.; Bottaro, J.; Highsmith, T.; Gilardi, R. J. Energet. Mater. **2001**, *19*, 277.

Distribution A: Public Release, Distribution unlimited



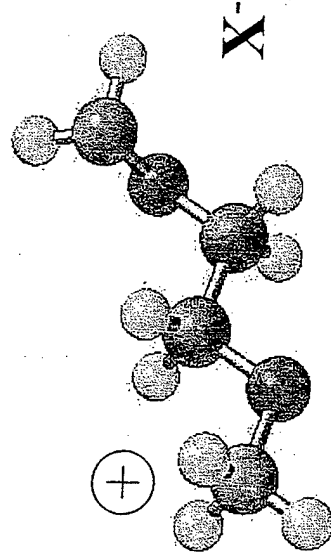
AFRL Ionic Liquids



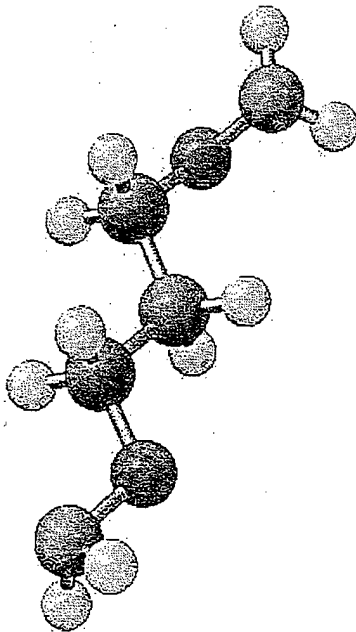
1,2-bis(oxyamine)ethane

Dixon, D. W.; Weiss, R. H. J Org. Chem. 1984,49, 4487.

H-X

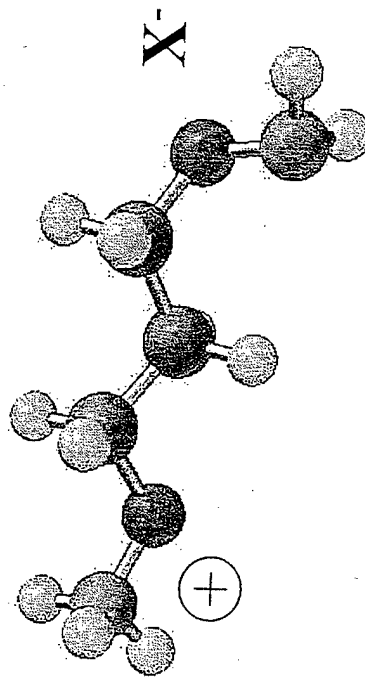


1,2-bis(oxyamine)ethane mono salts
 $X^- = NO_3^-, ClO_4^-, C(NO_2)_3^-, N(NO_2)_2^-$



1,3-bis(oxyamine)propane very stable, watery liquid
b.p. = 65-70 C @ 0.3 torr; f.p. = glasses at -40 C

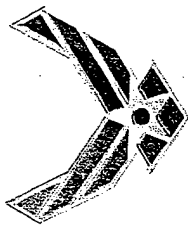
H-X



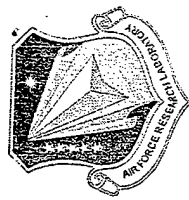
1,3-bis(oxyamine)propane mono salts
 $X^- = NO_3^-, ClO_4^-, C(NO_2)_3^-, N(NO_2)_2^-$

In either case, the oxyamines yield extremely friction and impact sensitive materials.

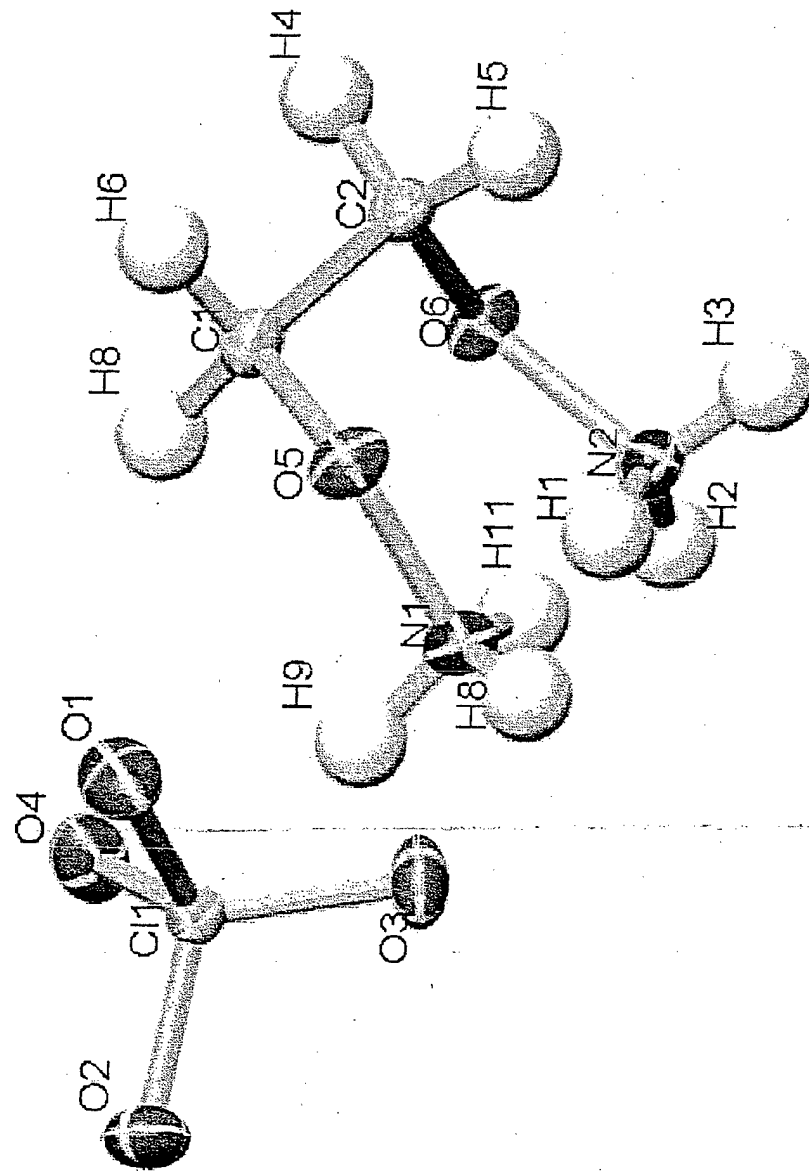
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.
"Distribution A: Public Release, Distribution unlimited"



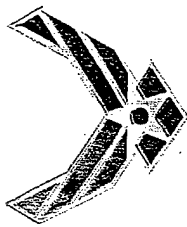
AFRL Ionic Liquids



X-ray diffraction confirmed structure, lots of hydrogen bonding!
H(1) and H(8) are partial occupancy 70%/30%



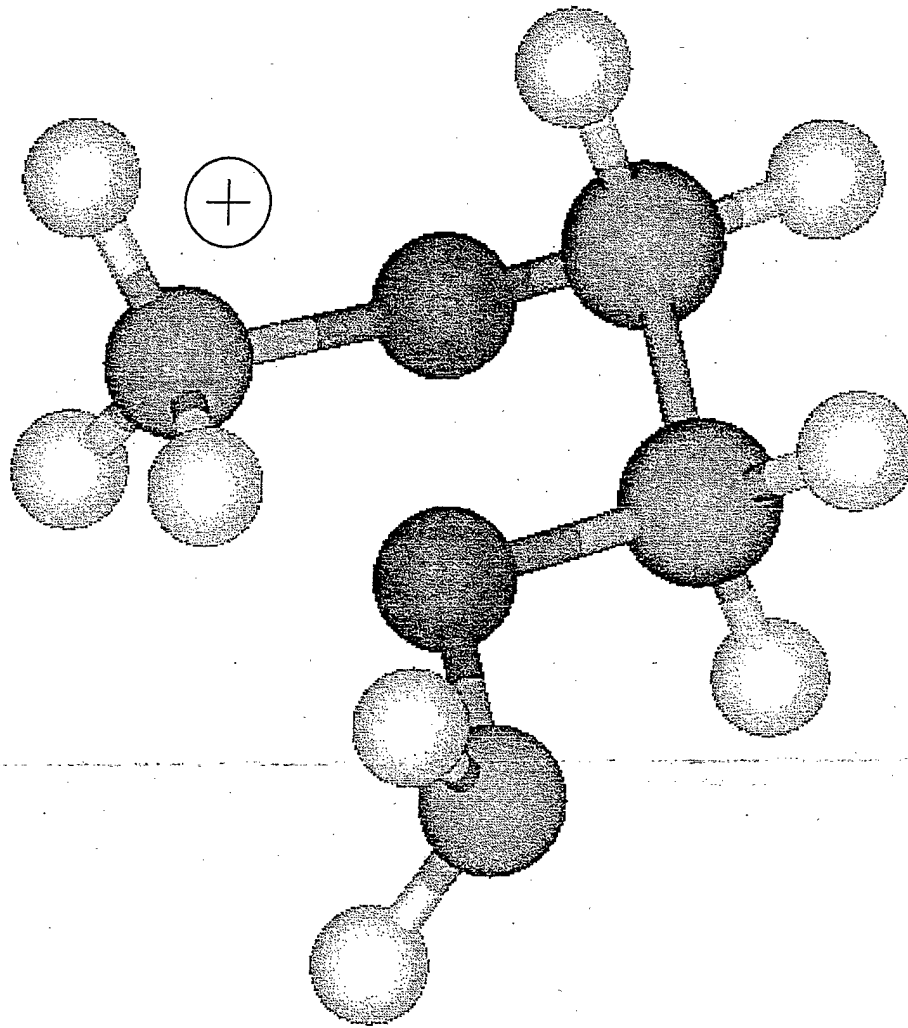
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.
Distribution A: Public Release, Distribution unlimited



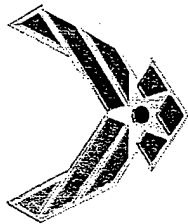
AFRL Ionic Liquids



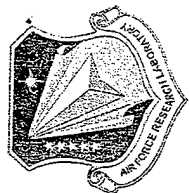
High level computational studies (Dr. Jeff Sheehy NASA/Marshall) revealed a slightly different structure. Comparison of bond distances matched well though



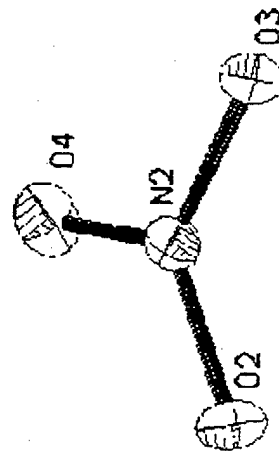
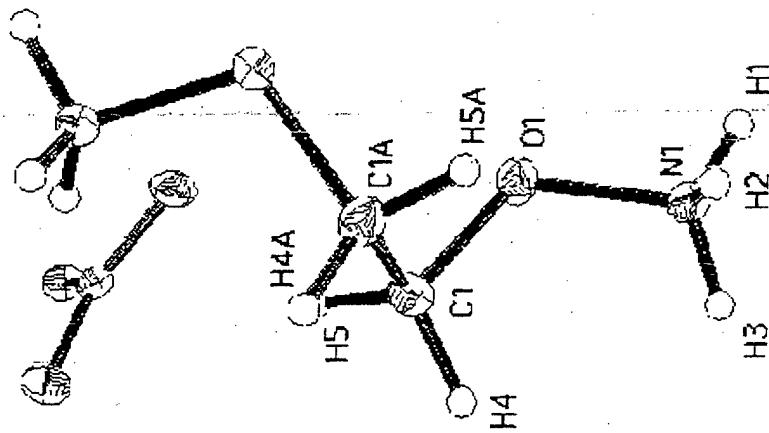
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.
Distribution A: Public Release, Distribution unlimited



AFRL Ionic Liquids

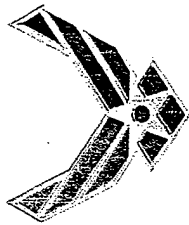


X-ray structure ethylene bisoxayamine dinitrate was also solved

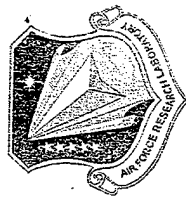


Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.

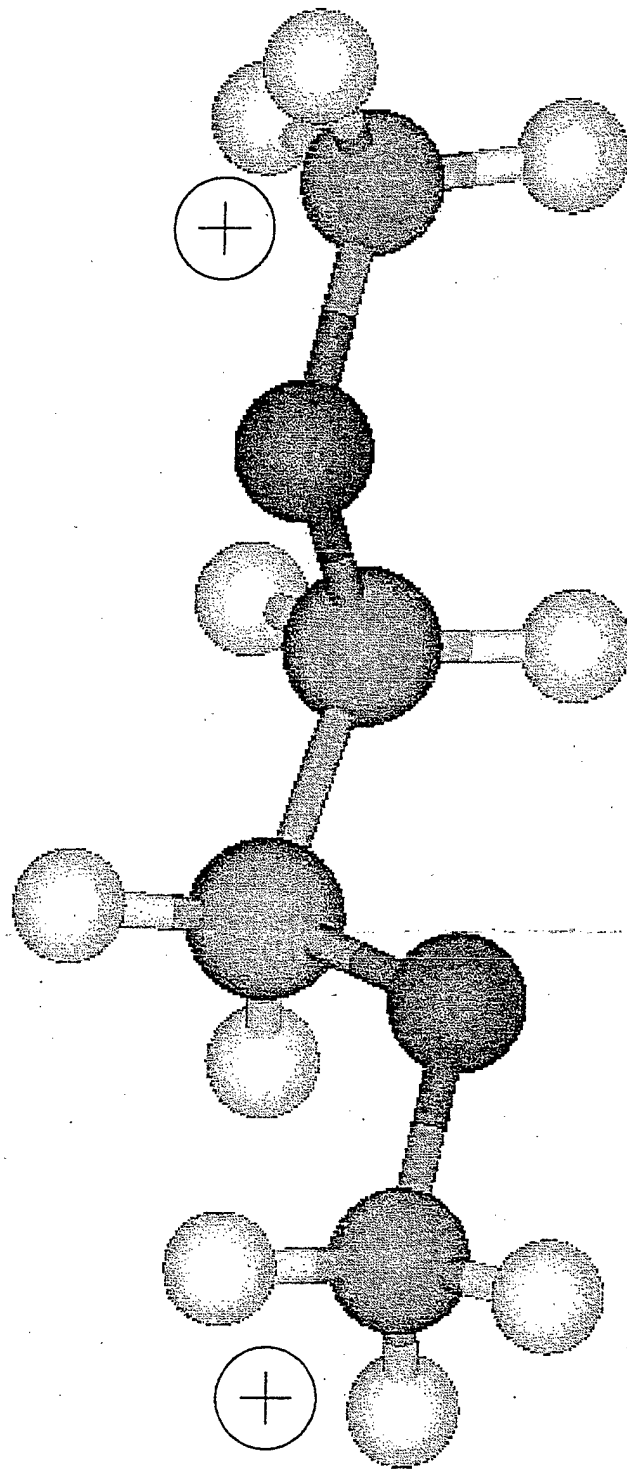
Distribution A: Public Release, Distribution unlimited



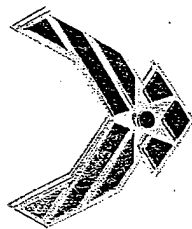
AFRL Ionic Liquids



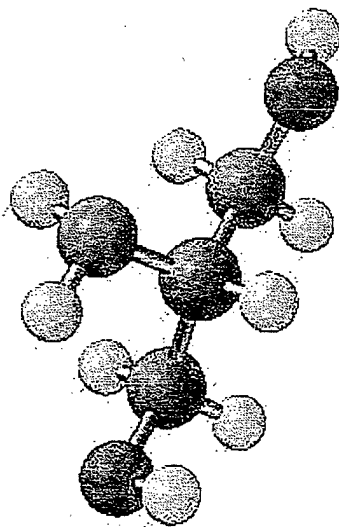
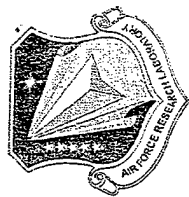
High level calculations (Jeff Sheehy) of the gas phase ethylene bisoxayammonium Dication revealed a similar structure with accurately predicted bond distances.



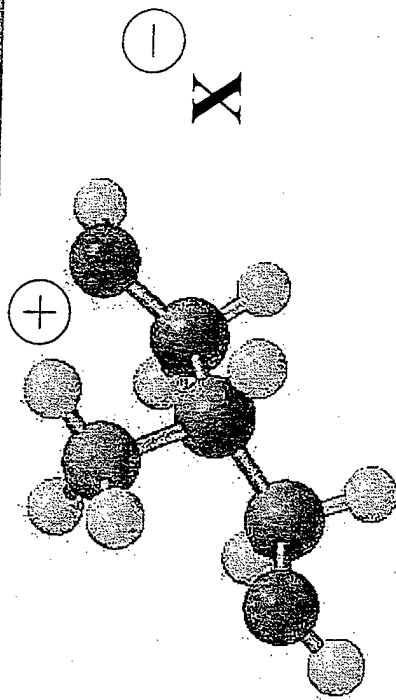
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.
Distribution A: Public Release, Distribution unlimited



AFRL Ionic Liquids



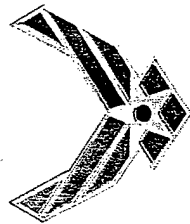
1,3-dihydroxy-2-aminopropane
(serinol)



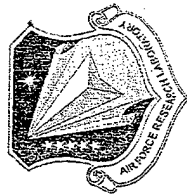
Salt	m.p.	DSC onset	Impact (kg-cm)	Friction (kg)
Serinol nitrate	61-66° C	215° C	180	18.0
Serinol perchlorate	55-60° C	250° C	200	>37.8
Serinol dinitramide	41-44° C	135° C	16	23.4

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. Prop. Energ. Pyrotech. 2004 submitted.

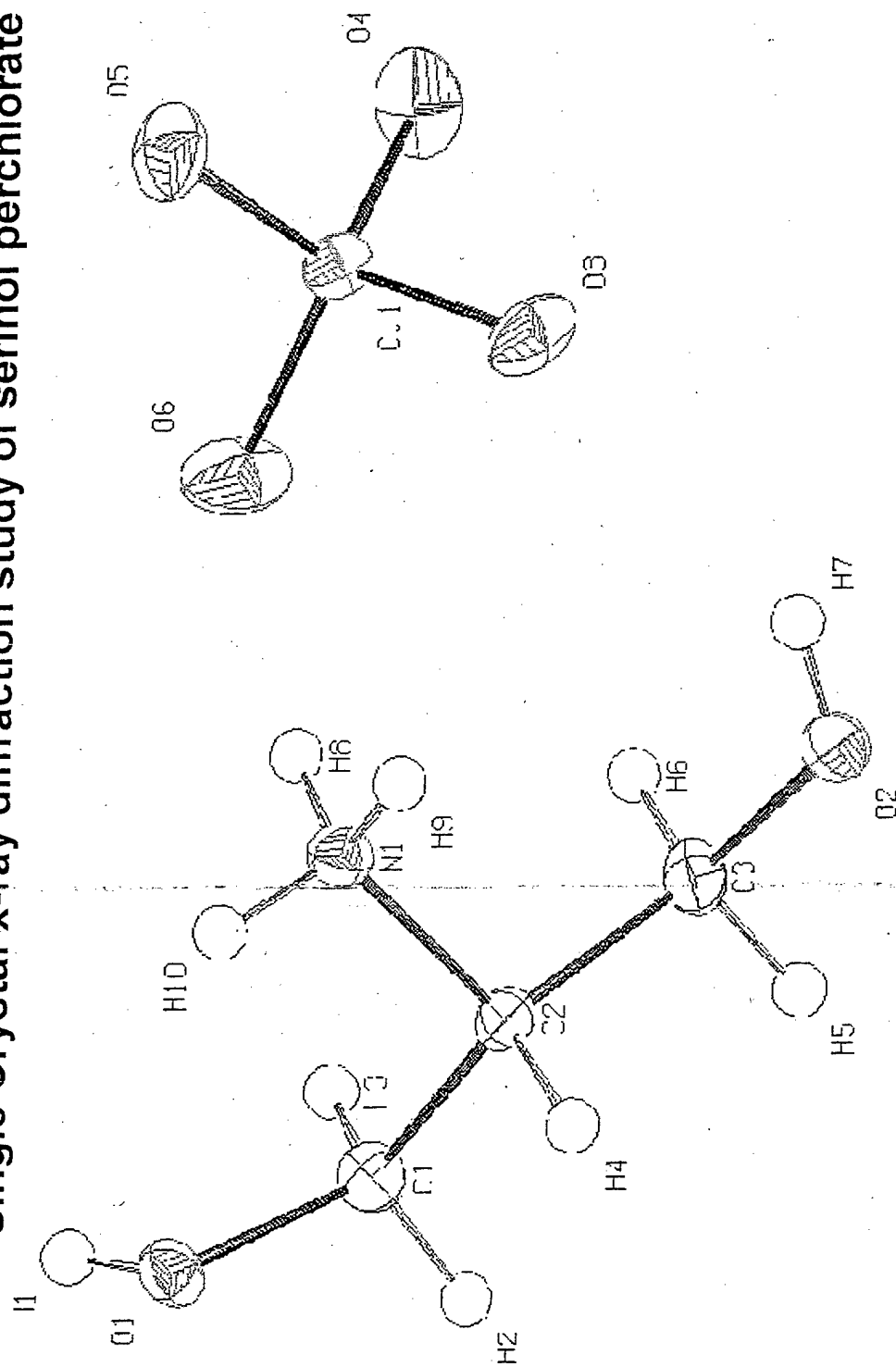
"Distribution A: Public Release, Distribution unlimited"

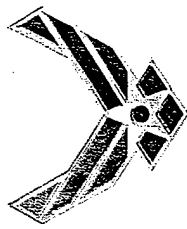


AFRL Ionic Liquids

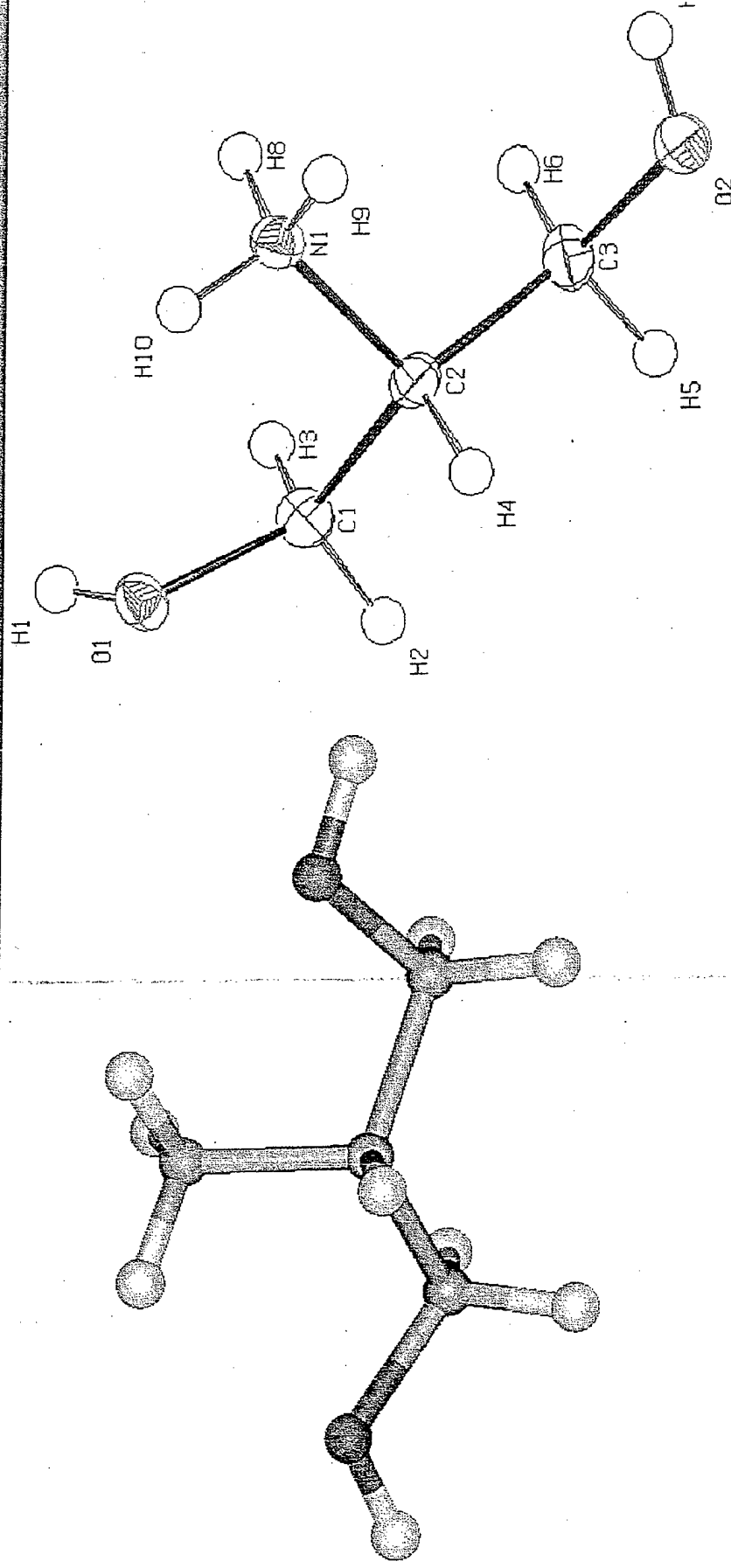


Single Crystal x-ray diffraction study of serinol perchlorate

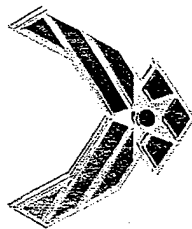




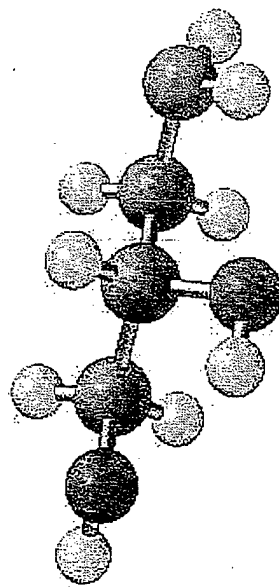
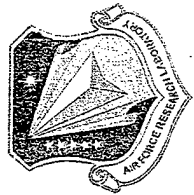
AFRL Ionic Liquids



Theoretical computations by Dr. Jerry Boatz (AFRL) using B3LYP/6-31G(d,p) of serinol cation in the gas phase (C_s symmetry) as compared to that observed in the single crystal x-ray diffraction study of serinol perchlorate

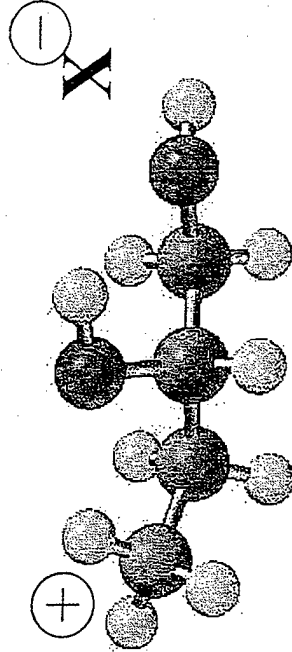


AFRL Ionic Liquids



1,2-dihydroxy-3-aminopropane
(chiral)

H-X

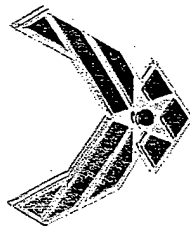


$X^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N}(\text{NO}_2)_2^-$

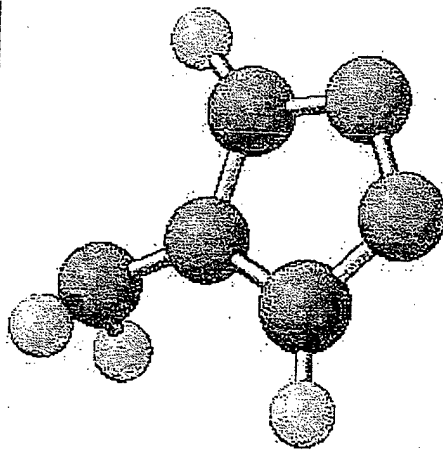
<u>SALT</u>	<u>Melting Point</u>	<u>Decomposition Onset</u>
1,2-dihydroxy-3-aminopropane nitrate	-40° C	220° C
1,2-dihydroxy-3-aminopropane perchlorate	?	225° C
1,2-dihydroxy-3-aminopropane dinitramide	-5° C	135° C

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. manuscript in progress, 2004.

Distribution A: Public Release, Distribution unlimited

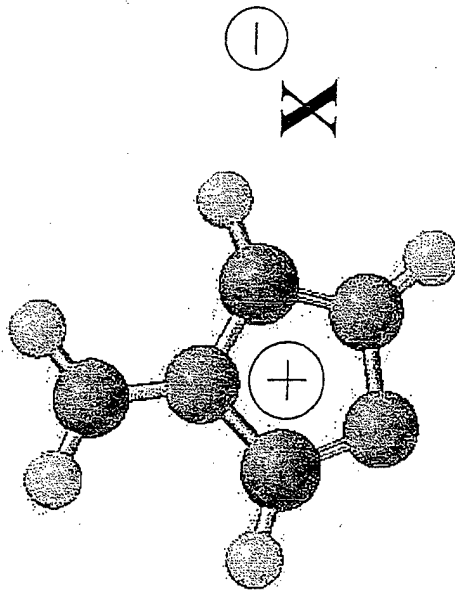


AFRL Ionic Liquids



4-amino-1,2,4-triazole

H-X



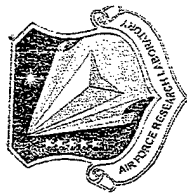
<u>SALT</u>	<u>Melting Point</u>	<u>Decomposition Onset</u>	<u>Impact</u> kgcm
4-amino-1,2,4-triazolium nitrate	69° C	180° C	>200
4-amino-1,2,4-triazolium perchlorate	84° C	210° C	30
4-amino-1,2,4-triazolium dinitramide	20° C	145° C	<5

Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; McKay, M.; Vij, A.; Ismail, I. Prop. Expl. Pyrotech. **2003**, 28, 174.

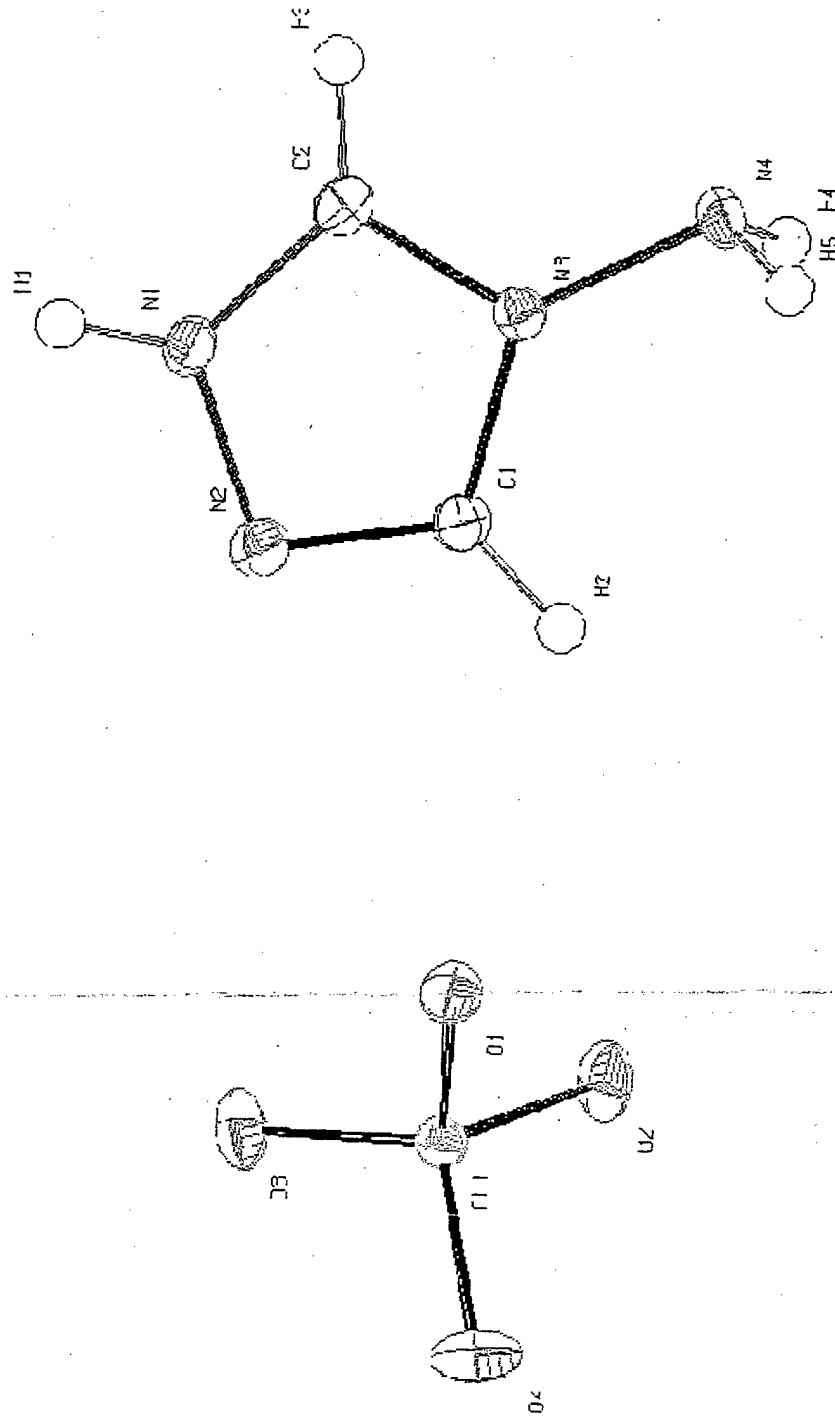
"Distribution A. Public Release, Distribution unlimited."



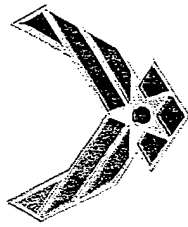
AFRL Ionic Liquids



Single crystal x-ray diffraction study revealed the expected structure for 4-amino-1,2,4-triazolium perchlorate.



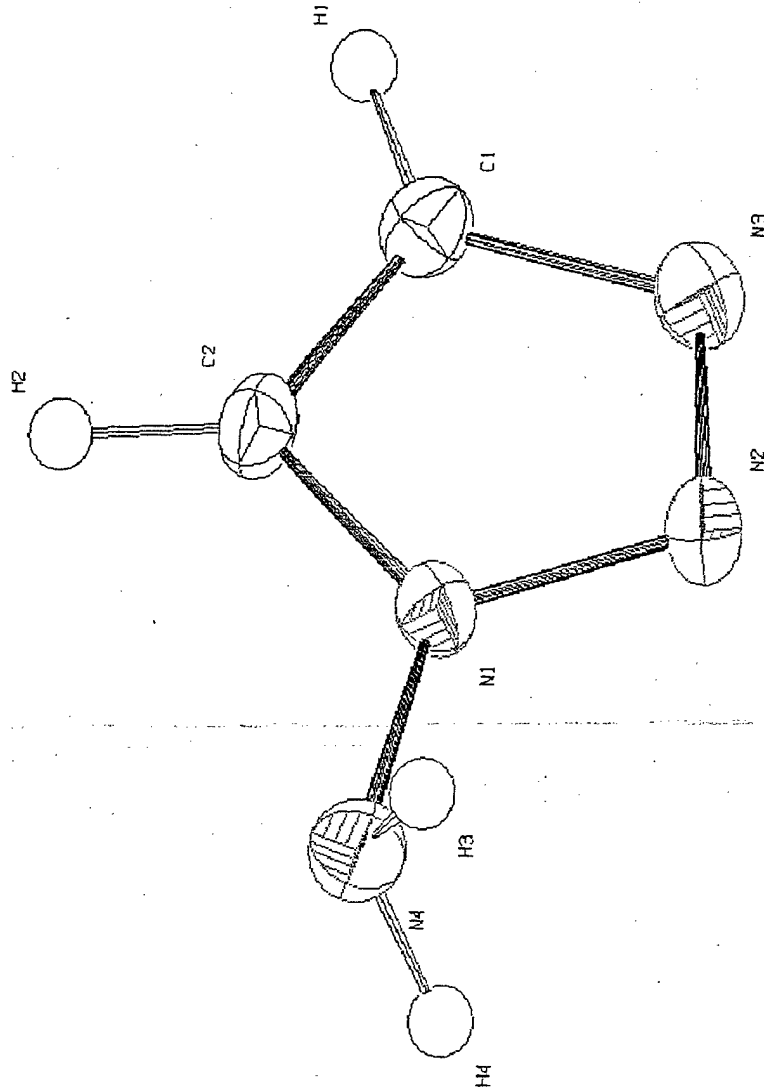
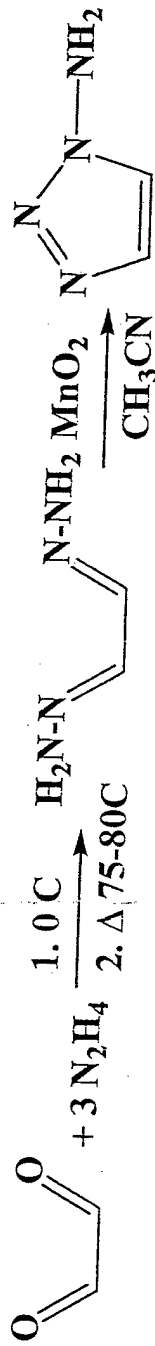
Hall, L.; Drake, G. Unpublished results 2004.
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids

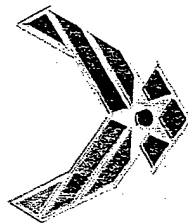


New Effort with 1-amino-1,2,3-triazole

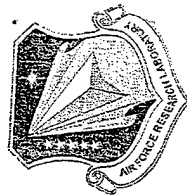


Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.

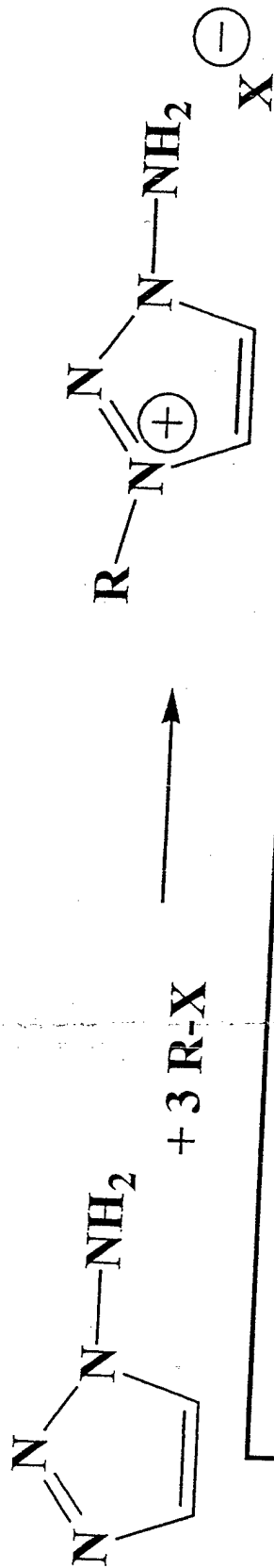
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids



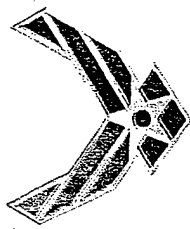
Synthesis of 1-amino-3-alkyl-1,2,3-triazolium halides



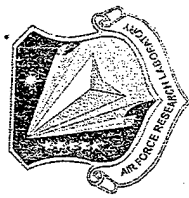
New Salt	M.P. (°C)	Decomp.
1-amino-3-methyl-1,2,3-triazolium iodide	146	150
1-amino-3-ethyl-1,2,3-triazolium bromide	118	149
1-amino-3-propyl-1,2,3-triazolium bromide	128	135
1-amino-3-allyl-1,2,3-triazolium bromide	100	135
1-amino-3-butyl-1,2,3-triazolium bromide	131	145

Not Ionic Liquids!

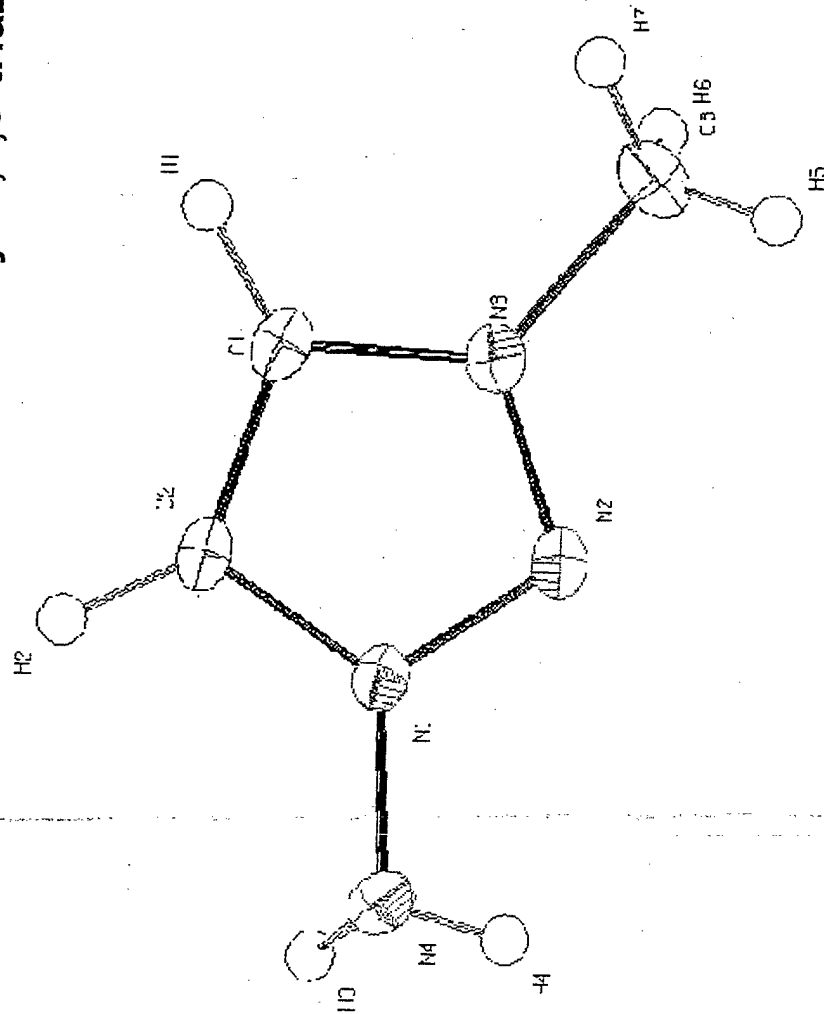
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. *J. Heterocyc. Chem.* submitted 2004.
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids

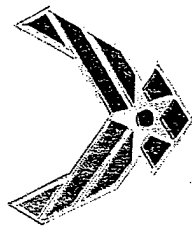


Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium iodide

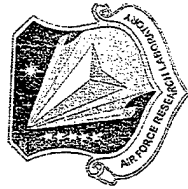


11

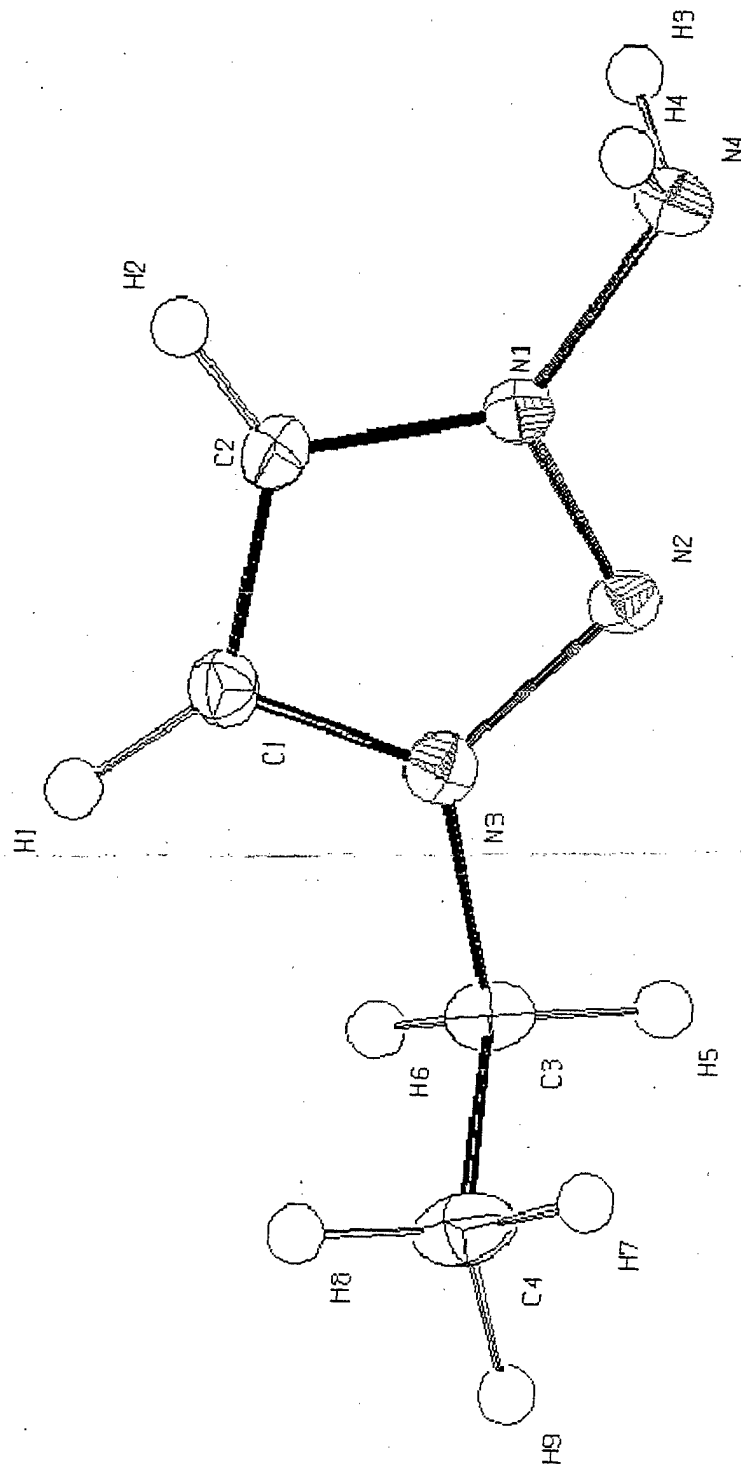
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids



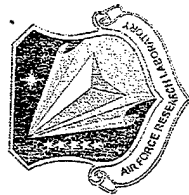
Single crystal x-ray diffraction study of 1-amino-3-ethyl-1,2,3-triazolium bromide



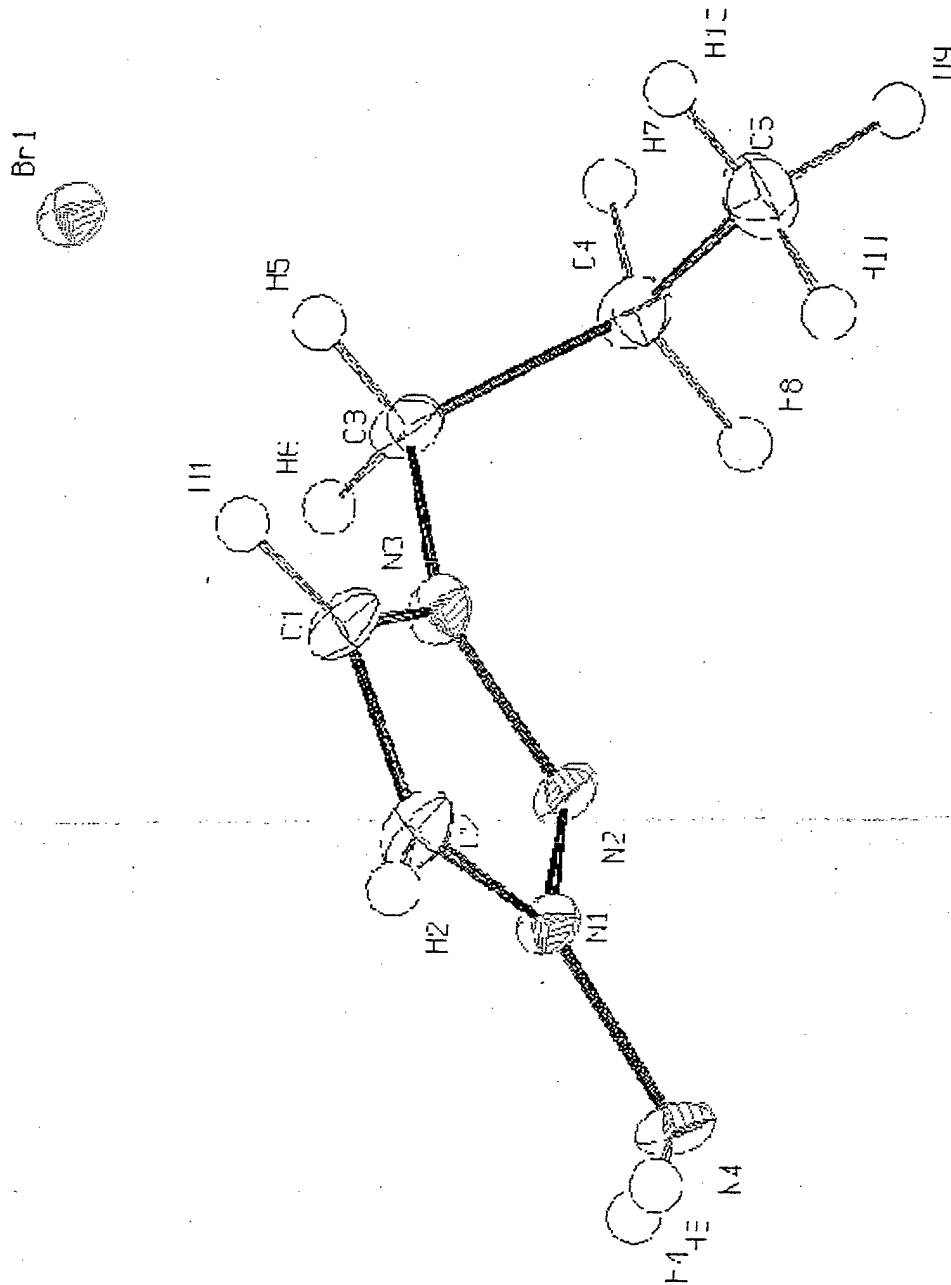
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
Distribution A. Public Release, Distribution unlimited



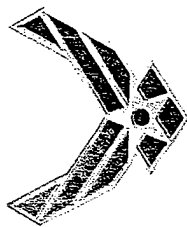
AFRL Ionic Liquids



Single crystal x-ray diffraction study of 1-amino-3-propyl-1,2,3-triazolium bromide



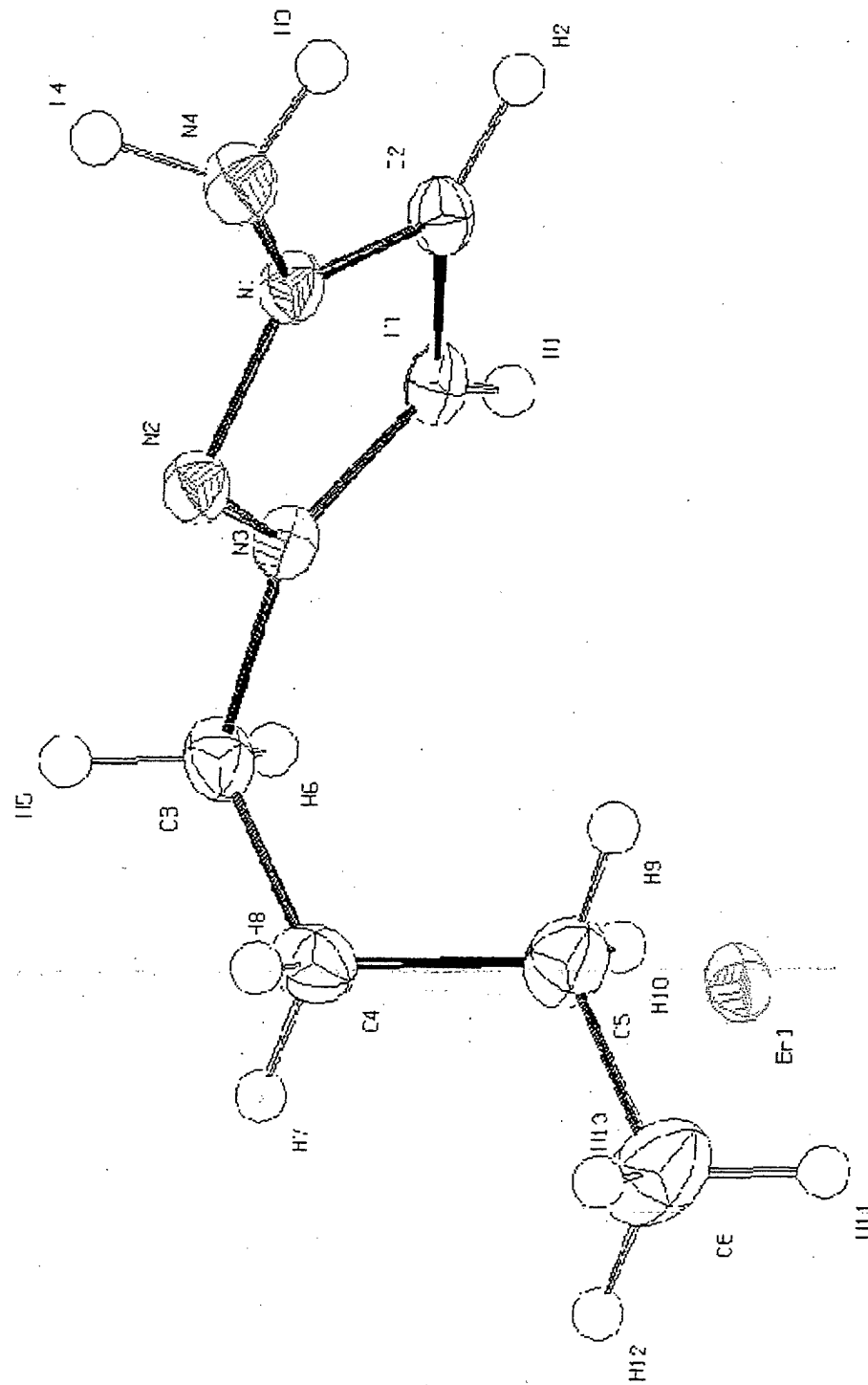
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids

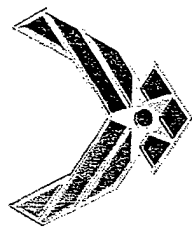


Single crystal x-ray structure of 1-amino-3-butyl-1,2,3-triazolium bromide



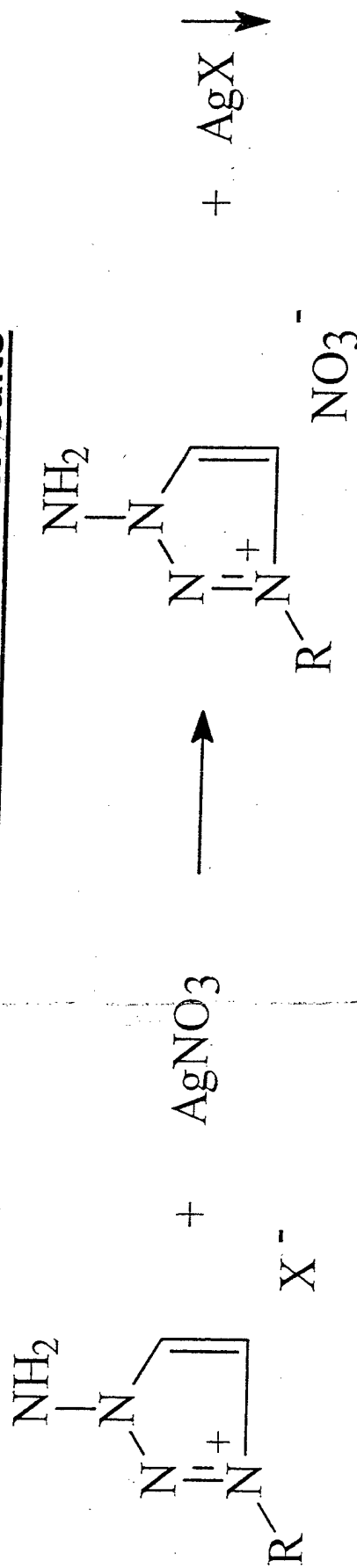
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. Heterocyc. Chem. submitted 2004.

Distribution A. Public Release, Distribution unlimited.



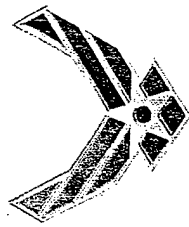
AFRL Ionic Liquids

Straight-forward metathesis forms desired nitrate salts



<u>NEW SALT</u>	M.P. ($^{\circ}\text{C}$)
1-amino-3-methyl-1,2,3-triazolium nitrate	86
1-amino-3-ethyl-1,2,3-triazolium nitrate	30
1-amino-3-propyl-1,2,3-triazolium nitrate	33
1-amino-3-allyl-1,2,3-triazolium nitrate	8
1-amino-3-butyl-1,2,3-triazolium nitrate	48

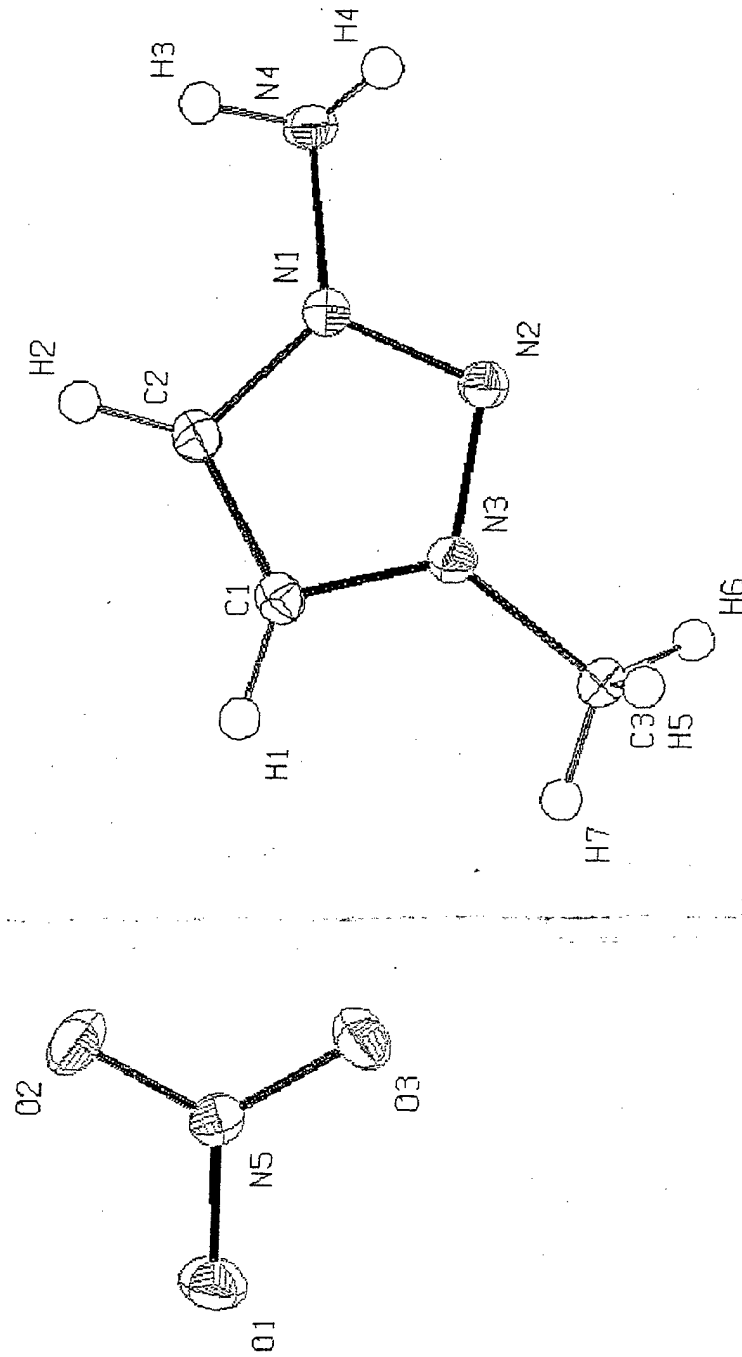
Kaplan, G.; Drake, G.; Tollison, K.; Hawkins, T.; Hall, L. Manuscript in progress 2004.
Distribution A. Public Release, Distribution unlimited.



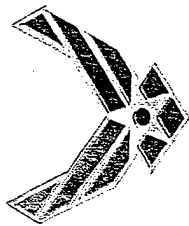
AFRL Ionic Liquids



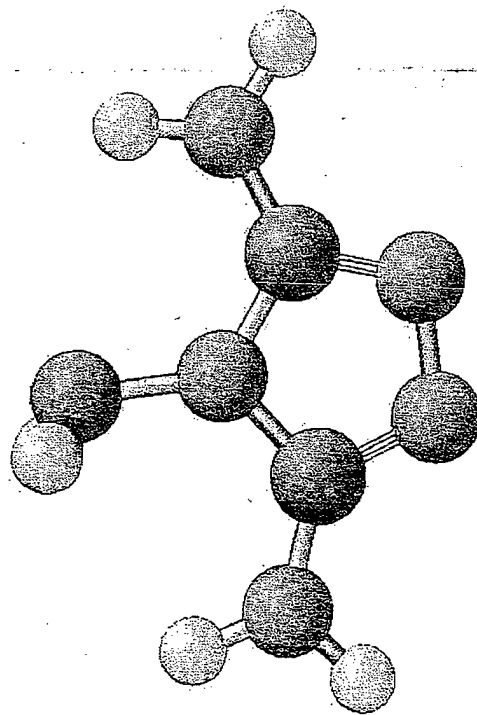
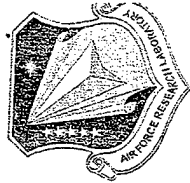
Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium nitrate



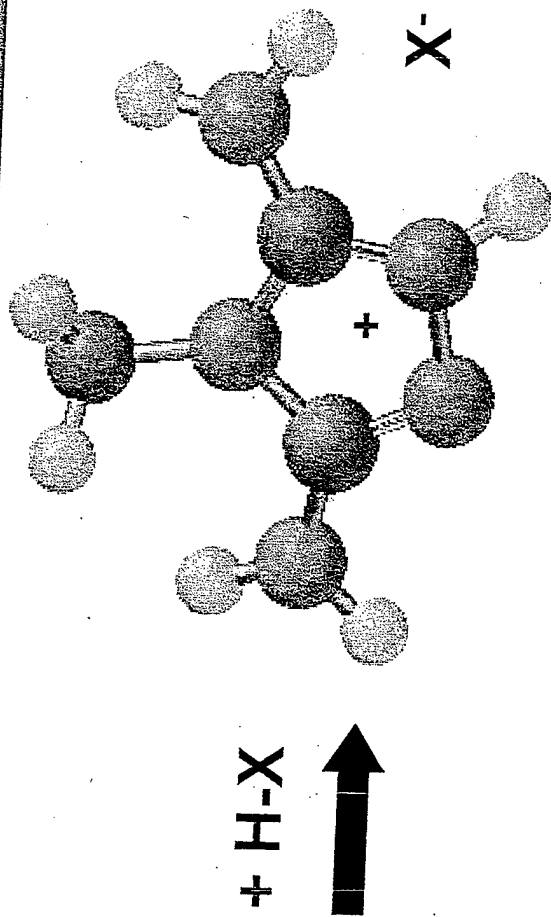
Kaplan, G.; Drake, G.; Hawkins, T.; Hall, L.; Tollison, K. Manuscript in progress 2004
Distribution A. Public Release, Distribution unlimited.



AFRL Ionic Liquids



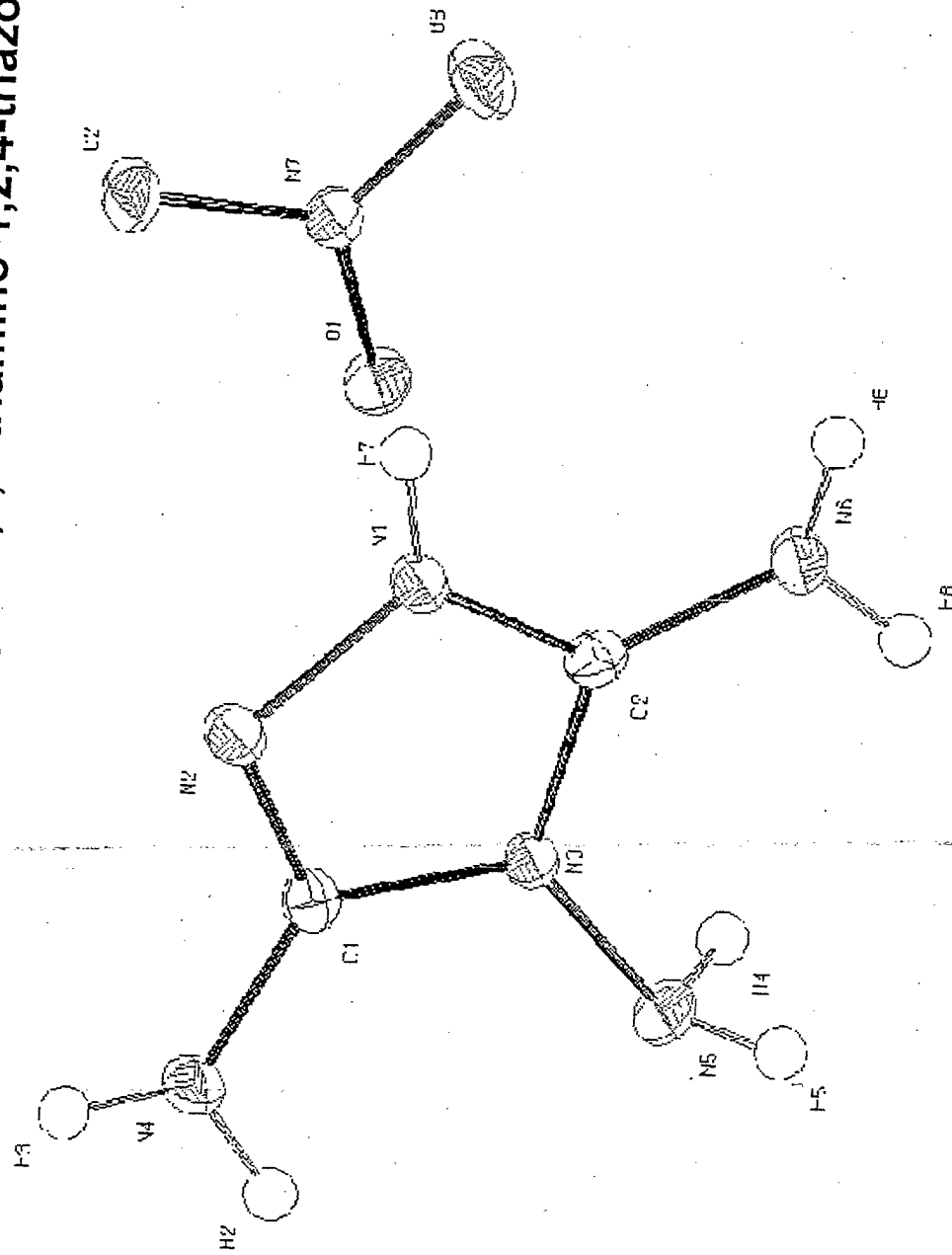
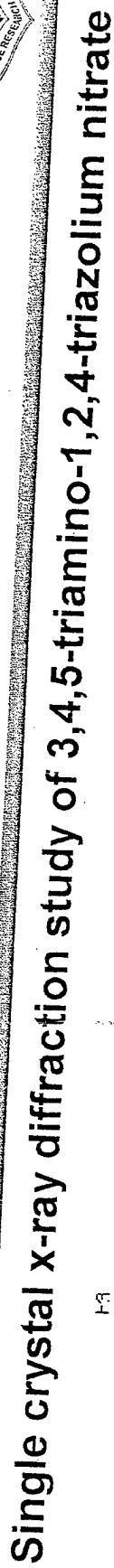
3,4,5-triamino-1,2,4-triazole
(Guanazine)



New Salt	M.P. (°C)	Impact (kgcm)	Friction (Kg)
Guanazinium nitrate	225	200	16
Guanazinium perchlorate	215	50	15.2
Guanazinium dinitramide	145	196	15.2

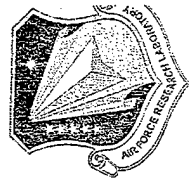
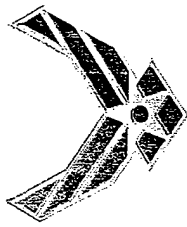
Not Ionic Liquids!

Drake, G.; Hawkins, T.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. 2004, to be submitted
Distribution A. Public Release, Distribution unlimited



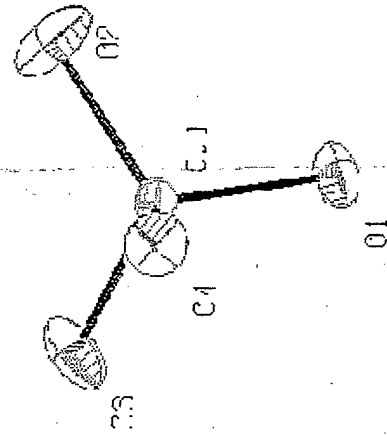
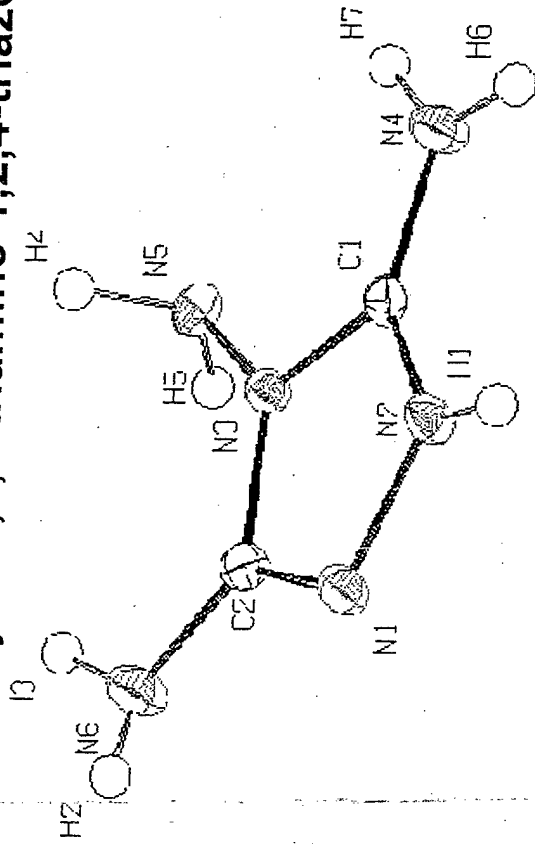
Drake, G.; Hawkins, T.; Hall, L.; Bränd, A. Prop. Expl. Pyrotech. **2004**, to be submitted

Distribution A. Public Release, Distribution unlimited

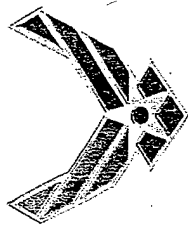


AFRL Ionic Liquids

Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium perchlorate



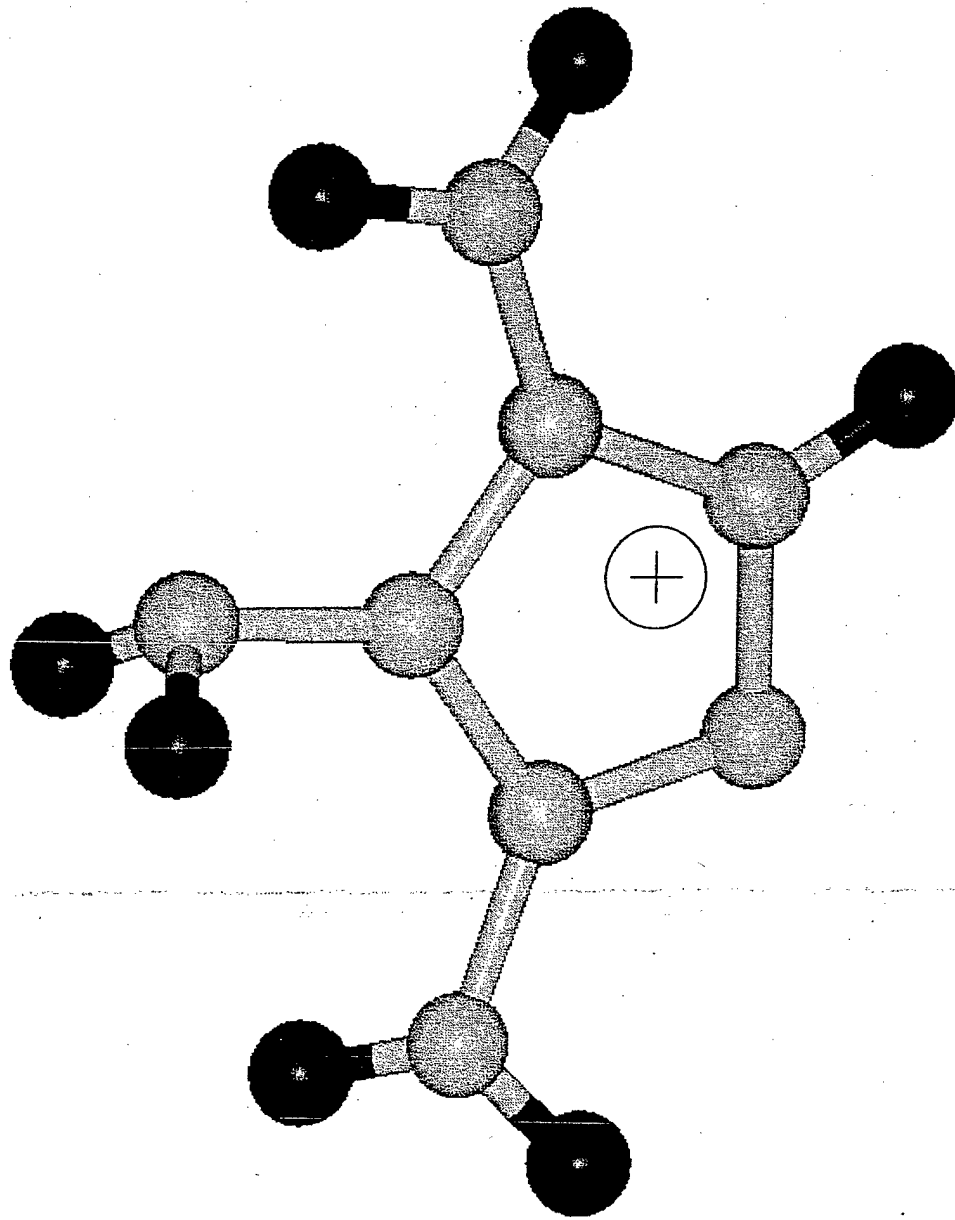
Drake, G.; Hawkins, T.; Boatz, J.; Hall, L.; Brand, A. *Prop. Expl. Pyrotech.* **2004**, to be submitted
Distribution A. Public Release, Distribution unlimited



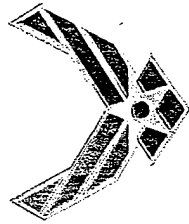
AFRL Ionic Liquids



Theoretical Calculations of protonated 3,4,5-triamino-1,2,4-triazole



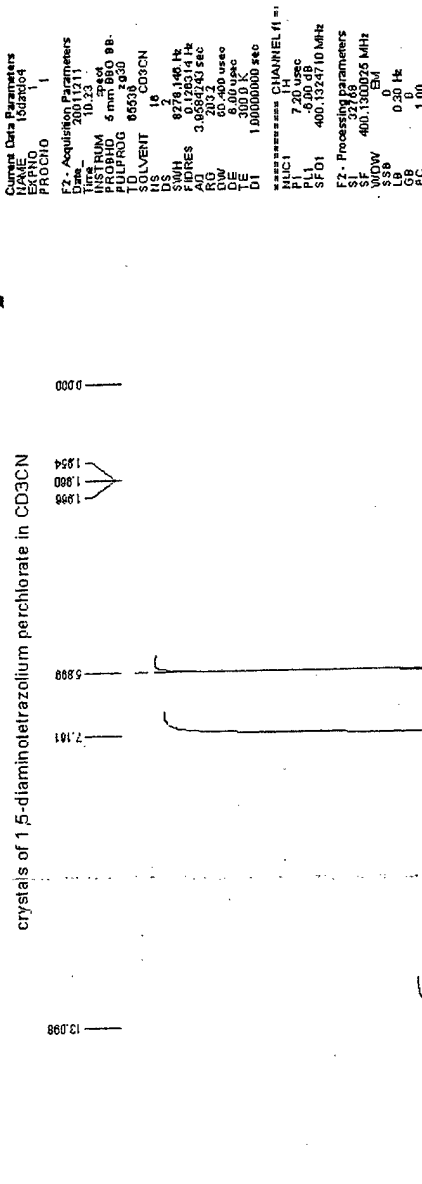
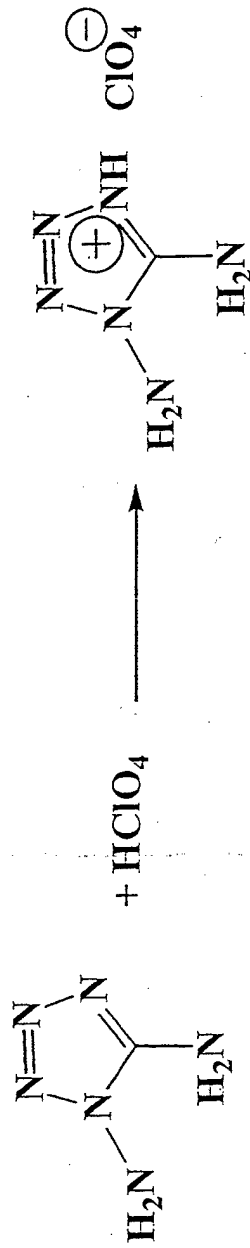
Drake, G.; Hawkins, T.; Boatz, J.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. **2004**, to be submitted
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids

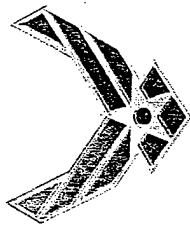


Experimental points to proton going on tetrazole ring, which disagrees from Russian findings



P. Gaponik; V. Karavai "Synthesis and properties of 1,5-diaminotetrazole" Khim. Geterotsikl. Soedin. 1984, 1683.

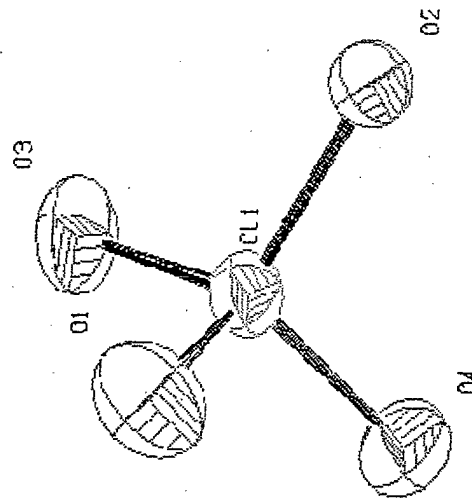
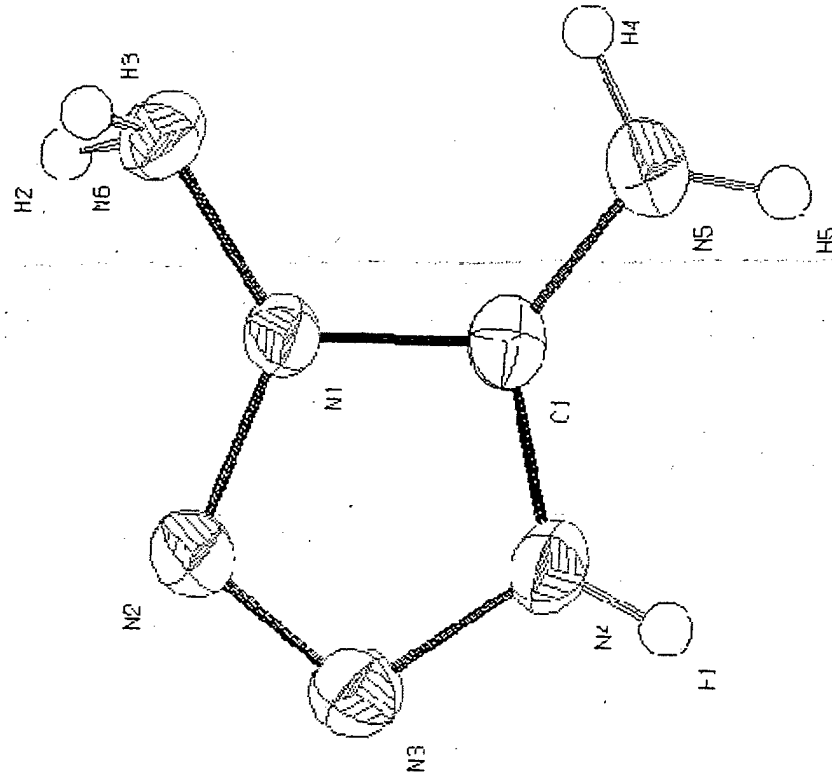
Distribution A. Public Release, Distribution unlimited



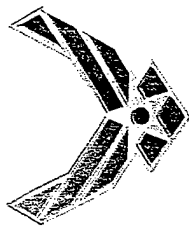
AFRL Ionic Liquids



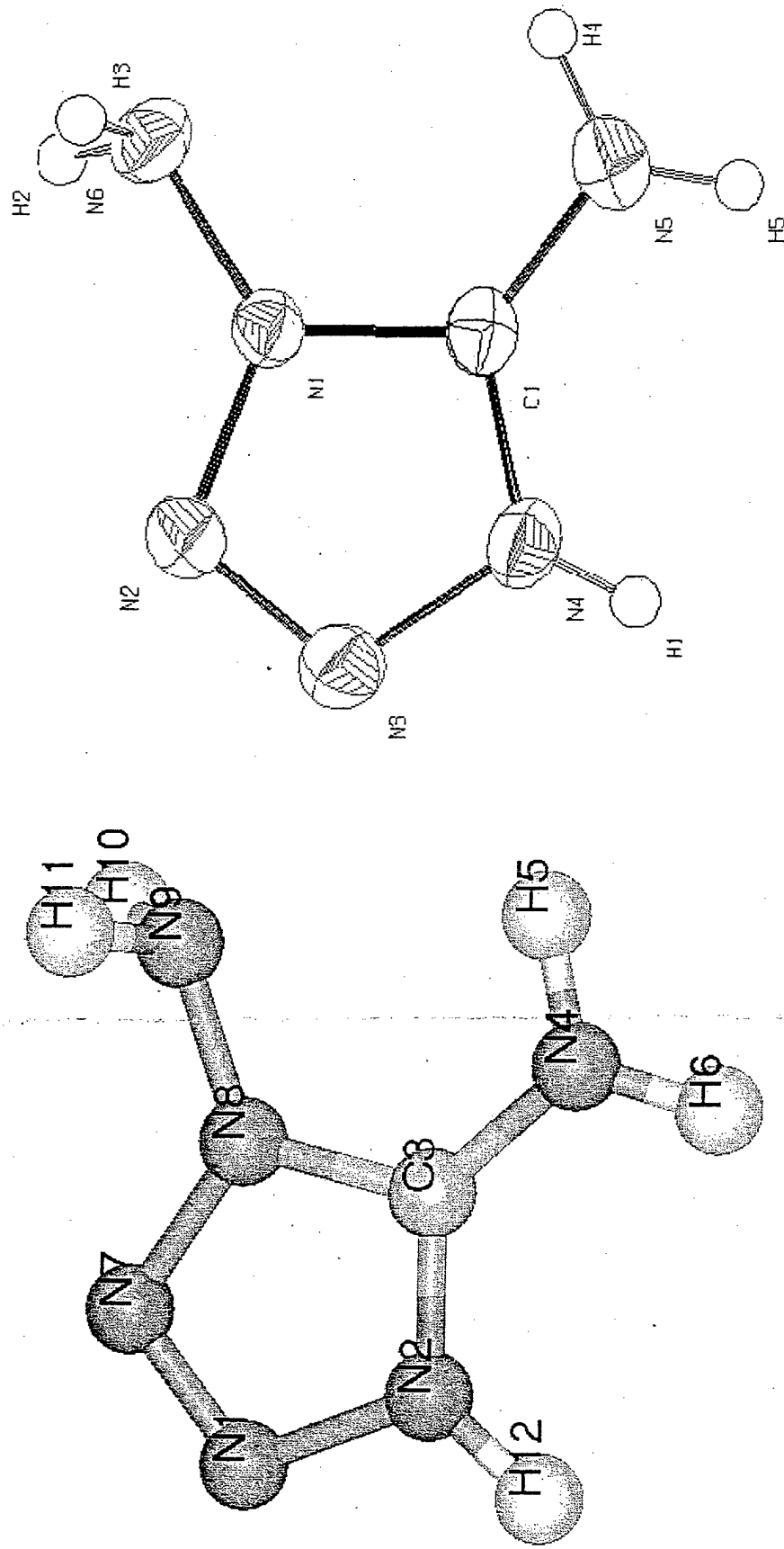
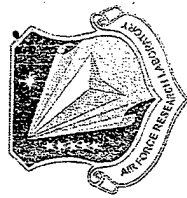
Single crystal x-ray diffraction study of 1,5-diamino-1,2,3,4-tetrazolium perchlorate



Drake, G.; Hawkins, T.; Vijj, A.; Hall, L.; Boatz, J. Prop. Explos. Pyro. **2004**, Submitted
Distribution A. Public Release, Distribution unlimited

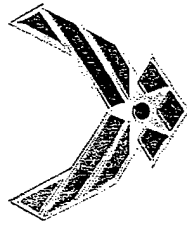


AFRL Ionic Liquids



Theory and Experimental Structures of 1,5-diamino-1,2,3,4-tetrazolium perchlorate
are in close agreement in distances and angles.

Drake, G.; Hawkins, T.; Vij, A.; Hall, L.; Boatz, J. *Prop. Explos. Pyro.* **2004**, Submitted
Distribution A. Public Release, Distribution unlimited



AFRL Ionic Liquids

Summary and Conclusions

Hydrogen bonding is highly important in all systems

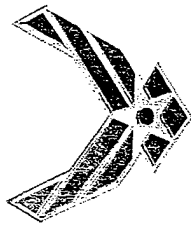
Asymmetry can dramatically affect physical properties and modest changes can have drastic affects.

N-amino heterocycles offer a rich platform for ionic liquids

New triazole and tetrazole systems have been identified as ionic liquid precursors

X-ray crystallography continues to be a powerful tool in identifying interactions in the solid state.

There are a lot of possibilities out there that await development....



AFRL Ionic Liquids

Acknowledgements

Mike Berman (AFOSR)

Mike Huggins (AFRL/PRS)

Adam Brand (AFRL/PRSP)

Ronald Channell (AFRL/PRSP)

Wayne Kalliomaas (AFRL/PRSP)

Brett Wight (ERC, Inc.)

Jeff Bottaro Mark Petrie (SRI Int.)